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Evaluation of Two Bisimide Additives in LARC-TPI Adhesive

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ABSTRACT

Recent studies at NASA-LaRC had shown that the processability of aromatic polyimides can be improved by the addition of bis(amide acids) or bisimides to LARC-TPI. These low molecular weight additives apparently lower the melt viscosity of aromatic polyimides without affecting their glass transition temperatures. Well-consolidated, fiber reinforced composites have been fabricated using this technology. LARC-TPI can be processed as a thermoplastic polyimide to form high strength bonds. However, this is generally accomplished by processing at relatively high bonding pressures, i.e., 2.07 MPa. This report covers the investigation of the effects of two bisimide additives to LARC-TPI adhesive in an attempt to improve the bonding process by lowering the viscosity of the material to achieve improved bond strength properties at lower bonding pressures. Results indicate some improvement in room temperature lap shear strength for the doped adhesives for the lowest bonding pressure, 0.34 MPa (50 psi), but some decrease in elevated temperature strength (232°C) for the C-PDA system. The C-PMDA system, bonded at 2.07 MPa (300 psi), exhibited comparable strengths to LARC-TPI after thermal and water boil exposures. Apparently, the high flow which is exhibited by the additive in the melt state, was not effective in lowering the overall viscosity because of the more viscous LARC-TPI.

1. INTRODUCTION

Recent work at NASA-Langley Research Center, has shown that the use of low molecular weight bis(amide acids) or bisimides is effective in lowering the viscosity of aromatic polyimides [1-4]. The improved processability of LARC-TPI with these additives or dopants has improved the fabrication of well-consolidated fiber-reinforced [4,5] composites as well as film processing and properties [2]. Although LARC-TPI has been processed as a thermoplastic polyimide to form lap shear bonds possessing high strengths, this is generally accomplished using high bonding pressures, 2.07 MPa (300 psi) [6]. Ideally, one would prefer to fabricate articles with minimal pressure, such as in the vacuum bag processing range, i.e., < 0.10 MPa (15 psi). Recent work has also shown that another method to achieve this is by controlling the molecular weight and the range of molecular weights by endcapping [7]. Our laboratory successfully bonded titanium to titanium lap shear specimens in a forced-air oven using vacuum bag pressure only with a controlled molecular weight material that is commercially available.

The purpose of this paper is to report on the investigation of the adhesive properties of bisimide doped LARC-TPI. The two bisimides investigated were aniline-pyromellitic dianhydride-aniline, identified as C-PMDA, and phthalic anhydride-p-phenylenediamine-phthalic anhydride, identified as C-PDA. The LARC-TPI versions doped with the additives are symbolically written as TPI/C-PMDA and TPI/C-PDA.

2. EXPERIMENTAL

2.1 Materials

The structures of LARC-TPI [6,8-10] and the bisimides, C-PMDA and C-PDA are shown in Fig. 1. LARC-TPI was manufactured and supplied by Mitsui Toatsu Chemicals, Incorporated, Tokyo, Japan, as a 29.1 wt. % solids poly(amid acid) solution in bis(2-methoxyethyl)ether (diglyme). The monomers used in the preparation were 3,3',4,4,'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone (3,3'-DABP). The solution, lot number 26-001, had an inherent viscosity (η_{inh}) of 0.49 dLg^{-1} (35°C) and a Brookfield viscosity of 24,600 cP (23°C).

An example of the preparation of the bis(amide acids) for the two bisimides, C-PMDA and C-PDA, are given in ref. 2 where C-PMDA is identified as An-PMDA-An and C-PDA as PA-pPDA-PA. Once the bis(amide acid) is prepared, it is converted to the bisimide by thermally treating for one hour at 300°C.

Preparation of the LARC-TPI doped with either of the bisimides, C-PMDA or C-PDA, was accomplished by adding the appropriate amount of the bisimide, as a powder, to the solution of LARC-TPI poly(amide acid) and thoroughly mixing until a slurry was obtained. The TPI/C-PMDA was prepared as a 2.5 wt. % solids of C-PMDA solution, whereas, the TPI/C-PDA was prepared as both a 2.5 and 5.0 wt. % solution of C-PDA.

2.2 Characterization

Lap shear strength (LSS) was determined according to ASTM D-1002 using an Instron Universal Testing Machine. The LSSs reported represent an average of four lap shear specimens per test condition except as noted in the tables. The range of LSSs is indicated by dashed lines in the bar graphs and is listed in the tables. Elevated temperature tests were conducted in a clam-shell, quartz-lamp oven with temperatures controlled to ± 3°C for all tests. Specimens were held 10 min at temperature prior to testing except for the water boil tests which were conducted upon reaching the test temperature (approximately 1-2 min).

Bondline thickness for the bonded titanium lap shear specimens is defined as the difference between the total joint thickness measured with a micrometer and the sum of the adherend thicknesses. The average bondline thickness for LARC-TPI lap shear specimens bonded at 0.34 MPa (50 psi) was 0.22 mm (8.7 mil) and 0.18

mm (7.0 mil) for those bonded at 1.38 MPa (200 psi). The average bondline thickness for the thermally aged and water boil specimens for TPI/C-PMDA [bonded at 2.07 MPa (300 psi)] was 0.08 mm (3.2 mil). Bondline thicknesses for the 2.5% and 5.0% C-PDA specimens ranged from 0.11 mm (4.5 mil) to 0.15 mm (5.8 mil) depending on the bonding pressure used.

Glass transition temperatures (Tg) of the adhesive from the fractured lap shear specimens were determined using a DuPont 990 Thermal Analyzer in conjunction with a DuPont Model 943 Thermal Mechanical Analyzer (TMA). TMAs were run in static air at a heating rate of 5°C/min using a hemispherical probe with a 15 g load.

Inherent viscosity was determined using a Cannon-Ubbelohde viscometer in a 35°C water bath controlled to within ± 0.01°C. A 10 ml solution of 0.5 wt/vol % solids in dimethylacetamide (DMAc) was made and filtered.

2.3 Preparation of adhesive tape

Adhesive tape for the LARC-TPI was prepared by brush coating a 7.5 wt % solids poly(amide acid) primer solution in diglyme onto 0.1 mm thick 112 E-glass cloth with an A-1100 finish (γ-aminopropylsilane). The glass cloth served as a carrier for the adhesive as well as a bondline control and an escape channel for solvent and volatile reaction products. After the first application was air-dried 30 min, a second application of the primer was air-dried for 1 h and heated in a forced-air oven for 1 h at each of three temperatures: 100, 150 and 175°C. The as-supplied 29.1 wt % solids solution was applied by pouring the resin on the glass cloth and spreading it with a reasonably stiff rubber squeegee until uniform. After each of several applications, the adhesive tape was exposed to the following schedule:

1. room temperature (RT) for 1 h;
2. RT $\rightarrow$ 75°C, hold 1 h;
3. 75 $\rightarrow$ 100°C, hold 1 h;
4. 100 $\rightarrow$ 150°C, hold 1 h; and
5. 150 $\rightarrow$ 175°C, hold 1 h.

This procedure was followed until a tape thickness of 0.20-0.28 mm (8-11 mil) was obtained. The rather involved procedure to prepare the tape was necessary to drive off solvent and reaction product volatiles when converting the poly(amide acid) to the polyimide.

Adhesive tapes for TPI/C-PDA (2.5%) and TPI/C-PDA (5.0%) were prepared in a similar manner. Some blistering occurred, making a tape thickness measurement meaningless.

Preparation of the adhesive tape for the TPI/C-PMDA (2.5%) was also similar except the heat treatment was as follows:

1. RT for 1 h;
2. RT $\rightarrow$ 75°C, hold 30 min;
3. 75° $\rightarrow$ hold 1 h;
4. 100 $\rightarrow$ 150°C, hold 2 h; and
5. 150 $\rightarrow$ 175°C, hold 3 h.

Some blistering also occurred for this tape preparation, however, thickness measurements were made where the area was free of blisters. The thickness was approximately 0.30 mm (12 mil).

2.4 Adhesive bonding

The prepared adhesive tapes were used to bond titanium adherends (Ti-6Al-4V, per Mil-T-9046E, Type III Comp) with a nominal thickness of 1.3 mm. The four-fingered

Ti-6Al-4V panels were grit blasted with 120 grit aluminum oxide, washed with methanol and treated with Pasa-Jell 107 to form a stable oxide on the surface. The adherends were washed with water and dried in a forced-air oven at 100°C for 5 min. The treated adherends were primed within two hours of the surface treatment by applying a thin coat of the respective adhesive solutions on the surfaces to be bonded. They were air-dried under a fume hood for 0.5 h, then placed in a forced-air oven and heated for 15 min at 100°C and 15 min at 150°C. The primed adherends were stored in a polyethylene bag and placed in a desiccator until needed. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 12.7 mm overlap (ASTM D-1002) and applying pressure in a hydraulic press. The bonding cycle used during this study was as follows.

1. Apply 0.34 MPa to 2.07 MPa pressure, heating rate ≈ 8°C min^{-1}, RT → 343°C or 371°C; hold 1 h;
2. Cool under pressure to ≈ 150°C and remove from bonding press.

2.5 Thermal and water boil exposure

A bonding cycle was selected for TPI/C-PMDA which was based on the highest LSSs produced and was used to prepare specimens to determine the effects of thermal exposure in a forced-air oven at 204°C ± 2°C for up to 5000 h. Lap shear strength tests were conducted at RT, 177, 204 and 232°C before (controls) and after exposures.

A 72-h water boil test was conducted in laboratory glassware containing boiling demineralized water. Lap shear specimens were immersed above the bonded area during the 72-h period. Lap shear strengths were determined at RT, 177, 204 and 232°C.

No thermal or water boil exposure tests were performed for the LARC-TPI or TPI/C-PDA.

3. RESULTS AND DISCUSSION

3.1 Chemistry

The proposed thermal reaction for the formation of LARC-TPI involves a polycondensation reaction where the poly(amide acid) formed from the monomers, BTDA and 3,3'-DABP, eliminates water in the formation of the polyimide.

The mechanisms proposed for how the bisimide additives operate to lower viscosity are given in ref. 4.

3.2 Bonding evaluation for TPI/C-PMDA

Recent studies have shown that improvement in bond strength is sometimes attained by further heat-treating the adhesive tape to high temperatures for a period of time.[11] Therefore, the TPI/C-PMDA adhesive tape previously heat-treated to 175°C was further heat-treated at 250°C for 1 h. Lap shear specimens were bonded at both 0.34 MPa (Fig. 2 and Table 1) and 2.07 MPa (Fig. 3 and Table 2). Successive heat treatments were also conducted at 275°C and 300°C and specimens bonded. Results are given in Fig. 2 and 3 and Tables 1 and 2.

The best LSS results for those bonded using 0.34 MPa pressure were obtained with the tape heat-treated to a maximum temperature of 175°C. Not given, but an indication of the flow obtained, was the increase in bonding thickness from 0.11 mm (4.3 mil) to 0.37 mm (14.7 mil) with increasing heat treatment temperature.

This indicates better flow was obtained for the lower temperature heat-treated adhesive tape.

Those bonded with 2.07 MPa pressure provided greater consistency in LSS values for all tape treatments and test temperatures. The differences in LSS for any one test temperature for the various heat treatments of the adhesive tapes fall within experimental error and therefore are insignificant. The bondline thickness for those bonded using 2.07 MPa bonding pressure varied very little, from 0.08 MPa (3.3 mil) to 0.11 MPa (4.5 mil). Those bonded using 2.07 MPa pressure with the tape heat-treated to 175°C maximum were chosen for thermal aging and water boil exposure because there were very little differences among all those bonded using 2.07 MPa pressure and because their LSS at 232°C was higher than those using the same tape bonded at 0.34 MPa pressure.

The types of failure, as determined by visual examination using a 10X magnification eyepiece, are given in Tables 1 and 2. Those specimens selected for thermal and water boil exposures exhibited cohesive failure for the four test temperatures.

Also given in the same tables are the Tgs determined by TMA on the adhesive from the fractured area of the tested specimens. The Tgs obtained indicated very little, if any, differences and therefore no trends were observed.

3.3 Bonding evaluation of LARC-TPI and TPI/C-PDA

The effect of bonding pressure on the LSSs was determined for LARC-TPI and TPI/C-PDA (2.5%) and (5.0%). Results are shown in Fig. 4 and given in Table 3 which includes the failure modes.

The LSSs for LARC-TPI, TPI/C-PDA (2.5%) and (5.0%) bonded at 1.38 MPa (200 psi) pressure are higher than their counterpart bonded at 0.34 MPa pressure for each test temperature except for those tested at 232°C for TPI/C-PDA (2.5%) and (5.0%) which are the same for each adhesive. LARC-TPI has essentially the same strength at RT (25.0 MPa) as TPI/C-PDA (2.5%) (25.1 MPa) and (5.0%) (26.1 MPa) but higher strengths at 177, 204 and 232°C. The expected improvement in adhesive properties with the addition of the C-PDA dopant is not evident. A possible explanation for this is a plasticization effect produced as a result of the additive which would result in lower strengths at elevated temperatures. The failure mode for the TPI/C-PDA (5.0%) adhesive tested at 232°C appeared to be a thermoplastic type of failure which indicates the possibility of the above mentioned effect. This type of failure was not evident for the LARC-TPI and TPI/C-PDA (2.5%) adhesives tested at 232°C.

3.4 Comparison of LARC-TPI and LARC-TPI with additives bonded using 0.34 MPa bonding pressure

Adhesive strengths of LARC-TPI, TPI/C-PMDA (2.5%), TPI/C-PDA (2.5%) and TPI/C-PDA (5.0%) bonded at 0.34 MPa pressure are compared in Fig. 5. All RT strengths are higher for the doped-LARC-TPIs than LARC-TPI, 17.6 MPa, with TPI/C-PMDA (2.5%) having the highest strength, 27.0 MPa. At 177°C, they are comparable with a range of 17.4 to 19.4 MPa. At 204°C, the LSS of TPI/C-PMDA (2.5%) is significantly higher than the other three, 19.6 MPa compared to 15.5 to 15.9 MPa. Again at 232°C, the TPI/C-PMDA (2.5%) has the highest strength, 12.9 MPa, slightly higher than LARC-TPI, 11.0 MPa, and significantly higher than TPI/C-PDA (2.5%) and (5.0%). Of the four systems bonded with 0.34 MPa pressure, TPI/C-PMDA provided the best results.

3.5 Thermal exposure

The effects on LSS due to thermal exposure in a forced-air oven at 204°C for TPI/C-PMDA (2.5%) adhesively bonded Ti-6Al-4V are shown in Fig. 6 and given in Table 4. LSS tests were performed at RT, 177, 204 and 232°C up to and including 5000 h exposure.

Slight decreases in LSS were noted with increasing time of thermal exposure. RT strength decreased from 27.7 MPa initially to 22.5 MPa after 5000 h exposure. After 5000 h exposure, the specimens retained 71, 77, 66 and 77% of the original strengths at RT, 177, 204 and 232°C, respectively. Therefore, the TPI/C-PMDA adhesive system shows respectable strength retention for up to at least 5000 h. The primary failure mode for all tested specimens was cohesive. Glass transition temperatures are also given in Table 4 and do not indicate any significant differences or trends.

3.6 72-h Water boil

Lap shear specimens were exposed to a 72-h water boil to determine the resistance of TPI/C-PMDA (2.5%) to a high humidity type condition. LSS test results are shown in Fig. 7 and given in Table 5.

The RT and 177°C LSS test results show essentially no differences due to the water exposure, however, only 50% and 32% of the original strength was retained at 204 and 232°C, respectively. Water is known to plasticize most polymers and, therefore, reduce their strength properties. All specimens failed cohesively. However, those specimens tested at 232°C failed thermoplastically indicating plasticization of the adhesive by the water.

4. SUMMARY

Previous reported studies in this laboratory have shown an improvement in processability of LARC-TPI by including either bis(amide acid) or bisimide additives in the polymer. The improvement was postulated to be due to the improved flow properties brought about by the introduction of low molecular weight additives which would interrupt the chain-to-chain interaction in the polymer, resulting in low melt viscosity.

LARC-TPI, a tough, thermooxidatively stable, flexible and solvent resistant polymer, can be processed as a thermoplastic polyimide with limited flow and, therefore, generally requires high processing pressures.

Based on the above mentioned studies, two bisimide additives, or dopants, prepared in our laboratory, C-PMDA and C-PDA, were added at a level of 2.5 and 5.0 wt % solids to the poly(amide acid) resin of LARC-TPI and evaluated as high temperature adhesives.

The lap shear strength (LSS) of adhesively bonded Ti-6Al-4V adherends was the primary consideration when evaluating the effect of the bisimide additives to the poly(amide acid) of LARC-TPI. Also noted was the type of failure, cohesive or interfacial, and in some cases, the effect on the Tg of the adhesive in the fractured area of the tested specimens.

Thermal exposure for the TPI/C-PMDA (2.5%) adhesive system at 204°C in a forced-air oven for up to and including 5000 h and a 72-h water boil were conducted on lap shear specimens. Tests were performed at RT, 177, 204 and 232°C before (controls) and after thermal exposure and water boil. Slight decreases in LSS were obtained with increasing time of thermal exposure. However, respectable strength retention was obtained for at least 5000 h at 204°C. Only 50% and 32% of the original strength was retained for tests at 204 and 232°C after the 72-h water boil.

Results of the study indicate that the bisimides, C-PMDA and C-PDA, when added to LARC-TPI, show a marked improvement in the RT LSS compared to the LARC-TPI RT LSS when bonded using 0.34 MPa bonding pressure. Also noted were no differences in strengths at 177, 204 and 232°C for C-PMDA and the same or decreased strengths for C-PDA at 177, 204 and 232°C. The lower strengths for the elevated temperature tests of the TPI/C-PDA system are possibly due to a plasticization effect or lowering of the Tg. This effect was not noted for the TPI/C-PMDA case.

The samples which contained the C-PMDA and bonded at 2.07 MPa exhibited strengths comparable to unmodified LARC-TPI after thermal and water boil exposure.

The improved processability and lower viscosity realized earlier for film and composite work with the bis(amide acid) and bisimides did not appear to significantly improve bond strengths for the bisimide doped LARC-TPI adhesives of this study except for the low pressure (0.34 MPa) bonded RT LSSs.

Future work will be directed towards producing a homogeneous blend of the additives with LARC-TPI. This will be accomplished by melting the two materials (additive and LARC-TPI) under high shearing forces in order to ensure homogenity which was not achieved in the present experiments.

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TABLE 1. RESULTS OF TPI/C-PMDA ADHESIVE TAPE HEAT TREATMENT FOR 0.34 MPa (50 PSI) BONDED Ti-6Al-4V

Bonding pressure MPa (psi)	Tape heat treatment	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[a]	Glass transition temperature, Tg[b] °C (°F)
0.34 (50)	175°C[c]	4	RT (RT)	27.0 (3920)	25.7-28.4 (3720-4120)	Co	234 (453)
		4	177 (350)	18.8 (2730)	16.8-20.3 (2440-2950)	Co	240 (464)
		4	204 (400)	19.6 (2840)	17.1-22.2 (2480-3220)	Co	232 (450)
		4	232 (450)	12.9 (1880)	12.1-14.1 (1760-2050)	Co	231 (448)
	Above plus 1 h at 200, 225, 250°C	4	RT (RT)	13.8 (2000)	13.4-14.4 (1940-2080)	I	233 (451)
		4	177 (350)	10.2 (1480)	9.6-10.5 (1400-1530)	I	235 (455)
		4	204 (400)	10.1 (1470)	9.4-10.7 (1360-1560)	I	234 (453)
		4	232 (450)	13.2 (1920)	11.5-14.9 (1680-2160)	Co[d]	230 (446)
	Above plus 1 h at 275°C	4	RT (RT)	11.7 (1700)	9.6-12.7 (1400-1840)	I	234 (453)
		4	177 (350)	9.3 (1350)	8.3-10.5 (1210-1530)	I	233 (451)
		4	204 (400)	9.0 (1300)	8.2-9.9 (1190-1440)	I	230 (446)
		4	232 (450)	10.3 (1490)	8.8-12.0 (1280-1740)	Co[d]	235 (455)
	Above plus 1 h at 300°C	4	RT (RT)	11.0 (1590)	10.1-12.7 (1460-1840)	Co	231 (448)
		4	177 (350)	8.8 (1270)	8.2-9.6 (1190-1390)	Co	239 (462)
		4	204 (400)	8.6 (1260)	8.0-10.1 (1160-1460)	Co	230 (446)
		4	232 (450)	10.0 (1450)	6.3-13.1 (910-1900)	Co[d]	235 (455)

Bonding conditions: heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 h.

[a] Co = cohesive; I = interfacial.

[b] Single measurement.

[c] Tape previously heated at 100°C, 1 h; 150°C, 2 h; 175°C, 3 h.

[d] Thermoplastic failure.

TABLE 2. RESULTS OF TPI/C-PMDA ADHESIVE TAPE HEAT TREATMENT FOR 2.07 MPa (300 PSI) BONDED Ti-6Al-4V

Bonding pressure MPa (psi)	Tape heat treatment	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[a]	Glass transition temperature, Tg[b] °C (°F)
2.07 (300)	175°C[c]	4	RT (RT)	27.7 (4020)	25.9-29.2 (3760-4240)	Co	240 (464)
		4	177 (350)	19.8 (2870)	18.6-20.6 (2700-3000)	Co	237 (459)
		4	204 (400)	19.6 (2840)	18.8-20.8 (2720-3020)	Co	235 (455)
		4	232 (450)	15.4 (2230)	15.3-15.5 (2220-2250)	Co	239 (462)
	Above plus 1 h at 200, 225, 250°C	4	RT (RT)	24.4 (3540)	23.6-25.4 (3420-3690)	Co	230 (446)
		4	177 (350)	19.7 (2860)	17.8-23.5 (2590-3400)	Co/I	235 (455)
		4	204 (400)	19.3 (2800)	17.0-21.0 (2460-3050)	Co	235 (455)
		4	232 (450)	16.0 (2320)	15.5-16.3 (2240-2370)	Co/I	232 (450)
	Above plus 1 h at 275°C	4	RT (RT)	25.5 (1700)	24.6-26.2 (3560-3800)	Co	235 (455)
		4	177 (350)	19.8 (2870)	19.0-20.3 (2850-2940)	Co	236 (457)
		4	204 (400)	18.9 (2740)	17.5-19.9 (2540-2890)	Co	235 (455)
		4	232 (450)	17.4 (2530)	17.0-18.2 (2460-2640)	Co	230 (446)
	Above plus 1 h at 300°C	4	RT (RT)	24.5 (3350)	23.2-25.4 (3370-3690)	Co	235 (455)
		4	177 (350)	17.5 (2540)	16.6-18.3 (2400-2660)	Co	239 (462)
		4	204 (400)	17.8 (2590)	17.0-19.3 (2460-2800)	Co	234 (453)
		4	232 (450)	16.8 (2430)	15.9-17.2 (2300-2500)	Co	232 (450)

Bonding conditions: heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 h.

[a] Co = cohesive; I = interfacial.

[b] Single measurement.

[c] Tape previously heated at 100°C, 1 h; 150°C, 2 h; 175°C, 3 h.

TABLE 3. EFFECT OF BONDING PRESSURE ON LAP SHEAR STRENGTH FOR LARC-TPI, TPI/C-PDA (2.5%) AND TPI/C-PDA (5.0%) BONDED Ti-6Al-4V

Adhesive	Bonding pressure MPa (psi)[a]	Bondline thickness mm (mil)	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[b]
LARC-TPI	0.34 (50)	0.22 (8.7)	4	RT (RT)	17.6 (2560)	14.6-19.3 (2120-2800)	Co
			3	177 (350)	19.4 (2820)	17.8-20.6 (2580-2990)	Co
			4	204 (400)	15.9 (2310)	14.3-17.3 (2080-2510)	Co
			3	232 (450)	11.0 (1600)	10.1-12.1 (1460-1760)	Co
	1.38 (200)	0.18 (7.0)	4	RT (RT)	25.0 (3620)	21.1-29.4 (3060-4260)	Co/I
			4	177 (350)	28.3 (4100)	25.4-29.8 (3690-4320)	Co
			4	204 (400)	24.3 (3520)	23.1-25.9 (3350-3760)	Co
			4	232 (450)	15.0 (2170)	12.9-16.8 (1870-2440)	Co
TPI/C-PDA (2.5%)	0.34 (50)	0.13 (5.3)	4	RT (RT)	21.9 (3180)	20.3-25.7 (2940-3740)	Co
			4	177 (350)	17.4 (2520)	16.3-18.8 (2360-2720)	Co
			4	204 (400)	15.5 (2250)	14.6-17.0 (2120-2460)	Co
			4	232 (450)	9.3 (1350)	8.2-10.8 (1190-1560)	Co
	1.38 (200)	0.11 (4.5)	4	RT (RT)	25.1 (3640)	23.7-26.8 (3440-3890)	Co
			4	177 (350)	22.3 (3230)	21.6-23.6 (3130-3430)	Co
			4	204 (400)	19.4 (2820)	19.0-19.8 (2750-2870)	Co
			4	232 (450)	9.6 (1400)	9.0-11.6 (1300-1680)	Co/I
TPI/C-PDA (5.0%)	0.34 (50)	0.15 (5.8)	4	RT (RT)	23.8 (3460)	22.4-25.1 (3250-3640)	Co
			4	177 (350)	19.3 (2800)	18.3-21.0 (2660-3040)	Co
			4	204 (400)	15.9 (2310)	15.0-17.4 (2180-2520)	Co
			4	232 (450)	6.8 (980)	6.1-7.0 (880-1100)	Co[c]
	1.38 (200)	0.12 (4.6)	4	RT (RT)	26.1 (3790)	25.1-27.6 (3640-4000)	Co
			4	177 (350)	22.3 (3240)	20.1-23.8 (2920-3460)	Co
			4	204 (400)	18.5 (2690)	17.8-20.1 (2580-2920)	Co
			4	232 (450)	6.0 (870)	5.5-7.3 (800-1060)	Co[c]

[a] Bonding temperature was 371°C (700°F), held 1 h.
[b] Co = cohesive; I = interfacial.
[c] Thermoplastic failure.

TABLE 4. LSS TEST RESULTS OF THERMAL EXPOSURE AT 204°C FOR TPI/C-PMDA ADHESIVE BONDED Ti-6Al-4V

Time of exposure at 204°C (400°F) h	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[a]	Glass transition temperature, Tg[b] °C (°F)
0	4	RT (RT)	27.7 (4020)	25.9-29.2 (3760-4240)	Co	240 (464)
(Control)	4	177 (350)	19.8 (2870)	18.6-20.6 (2700-3000)	Co	237 (459)
	4	204 (400)	19.6 (2840)	18.8-20.8 (2720-3020)	Co	235 (455)
	4	232 (450)	15.4 (2230)	15.3-15.5 (2220-2250)	Co	239 (462)
1000	4	RT (RT)	26.8 (3890)	25.8-28.0 (3750-4070)	Co	235 (455)
	4	177 (350)	16.8 (2440)	15.9-17.8 (2310-2580)	Co	246 (475)
	4	204 (400)	14.3 (2070)	13.8-14.9 (2000-2160)	Co	243 (469)
	4	232 (450)	14.4 (2090)	12.7-15.8 (1850-2300)	Co	243 (469)
2000	4	RT (RT)	24.4 (3540)	23.6-25.2 (3420-3650)	Co	249 (480)
	4	177 (350)	16.2 (2350)	15.3-17.4 (2220-2520)	Co	252 (486)
	4	204 (400)	13.4 (1950)	12.6-13.8 (1840-2000)	Co	237 (459)
	4	232 (450)	11.5 (1670)	10.3-12.6 (1500-1830)	Co	245 (473)
5000	4	RT (RT)	22.5 (3260)	21.6-23.3 (3130-3380)	Co	248 (478)
	4	177 (350)	15.2 (2210)	14.3-16.5 (2080-2400)	Co	253 (487)
	4	204 (400)	13.0 (1890)	12.5-13.4 (1820-1940)	Co	245 (473)
	4	232 (450)	11.8 (1720)	11.0-12.5 (1600-1810)	Co	249 (480)

Bonding conditions: tape heated to max. 175°C for 3 h; 2.07 MPa (300 psi) pressure, heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 h.

[a] Co = cohesive.

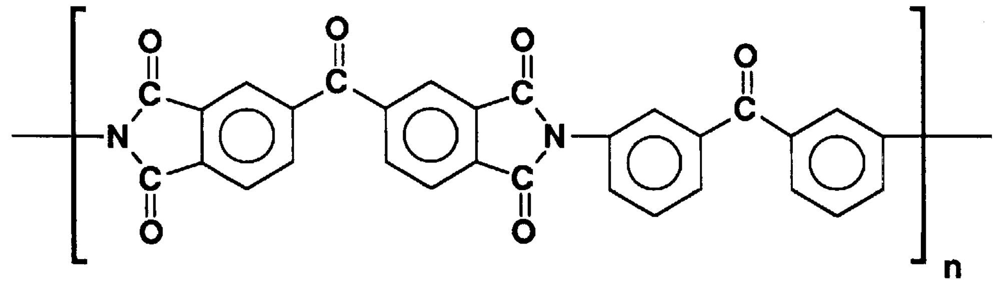
[b] Single measurement.

TABLE 5. LSS TEST RESULTS OF A 72-HOUR WATER BOIL FOR TPI/C-PMDA ADHESIVE BONDED Ti-6Al-4V

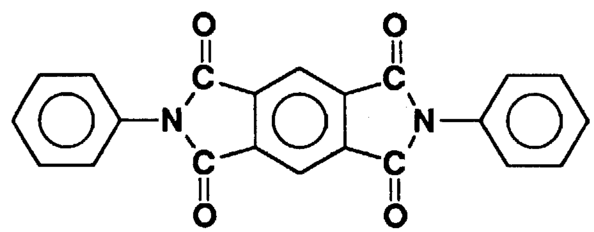
	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[a]	Glass transition temperature, Tg[b] °C (°F)
Control	4	RT (RT)	27.7 (4020)	25.9-29.2 (3760-4240)	Co	240 (464)
	4	177 (350)	19.8 (2870)	18.6-20.6 (2700-3000)	Co	237 (459)
	4	204 (400)	19.6 (2840)	18.8-20.8 (2720-3020)	Co	235 (455)
	4	232 (450)	15.4 (2230)	15.3-15.5 (2220-2250)	Co	239 (462)
72-hour water boil	4	RT (RT)	26.2 (3800)	24.4-27.3 (3540-3960)	Co	238 (460)
	4	177 (350)	17.9 (2600)	16.4-18.4 (2380-2680)	Co	234 (453)
	4	204 (400)	11.0 (1600)	10.3-12.0 (1500-1740)	Co	229 (444)
	4	232 (450)	5.0 (720)	4.6-5.4 (660-780)	Co[c]	234 (453)

Bonding conditions: tape heated to max. 175°C (347°F) for 3 h; heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 h.

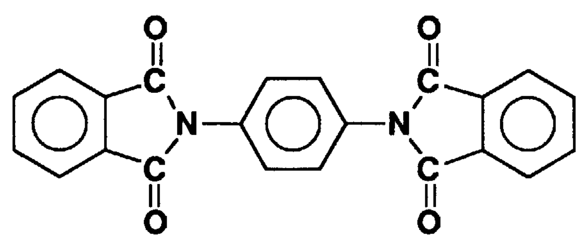
[a] Co = cohesive.
[b] Single measurement.
[c] Thermoplastic failure.



LARC-TPI

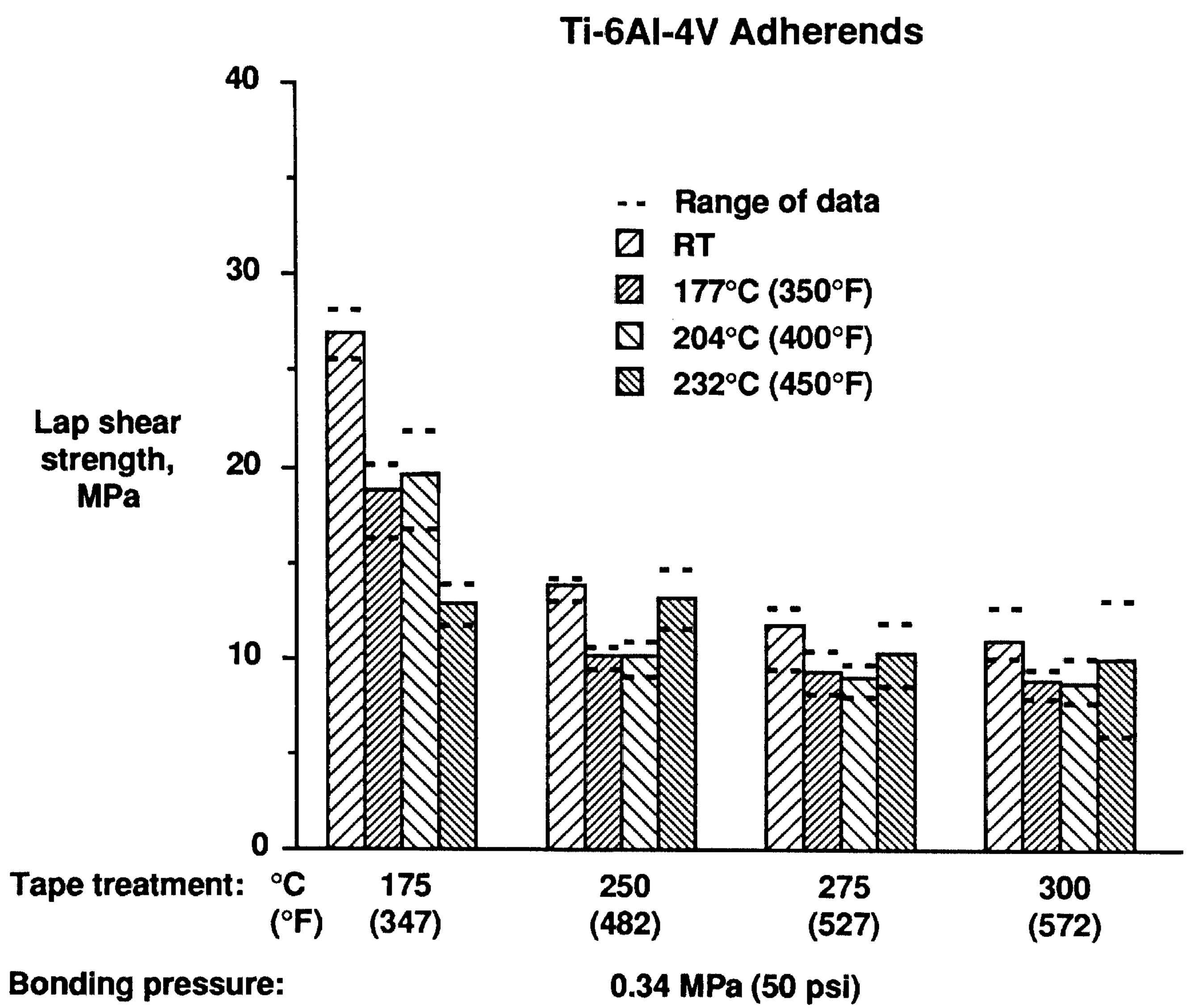


C-PMDA



C-PDA

FIGURE 1. STRUCTURE OF LARC-TPI AND DOPANTS C-PMDA AND C-PDA.



Cure : 343°C (650°F), 1 h

FIGURE 2. THE EFFECT OF TAPE HEAT TREATMENT PRIOR TO BONDING WITH 0.34 MPa (50 PSI) PRESSURE FOR TPI/C-PMDA BONDED Ti-6Al-4V.

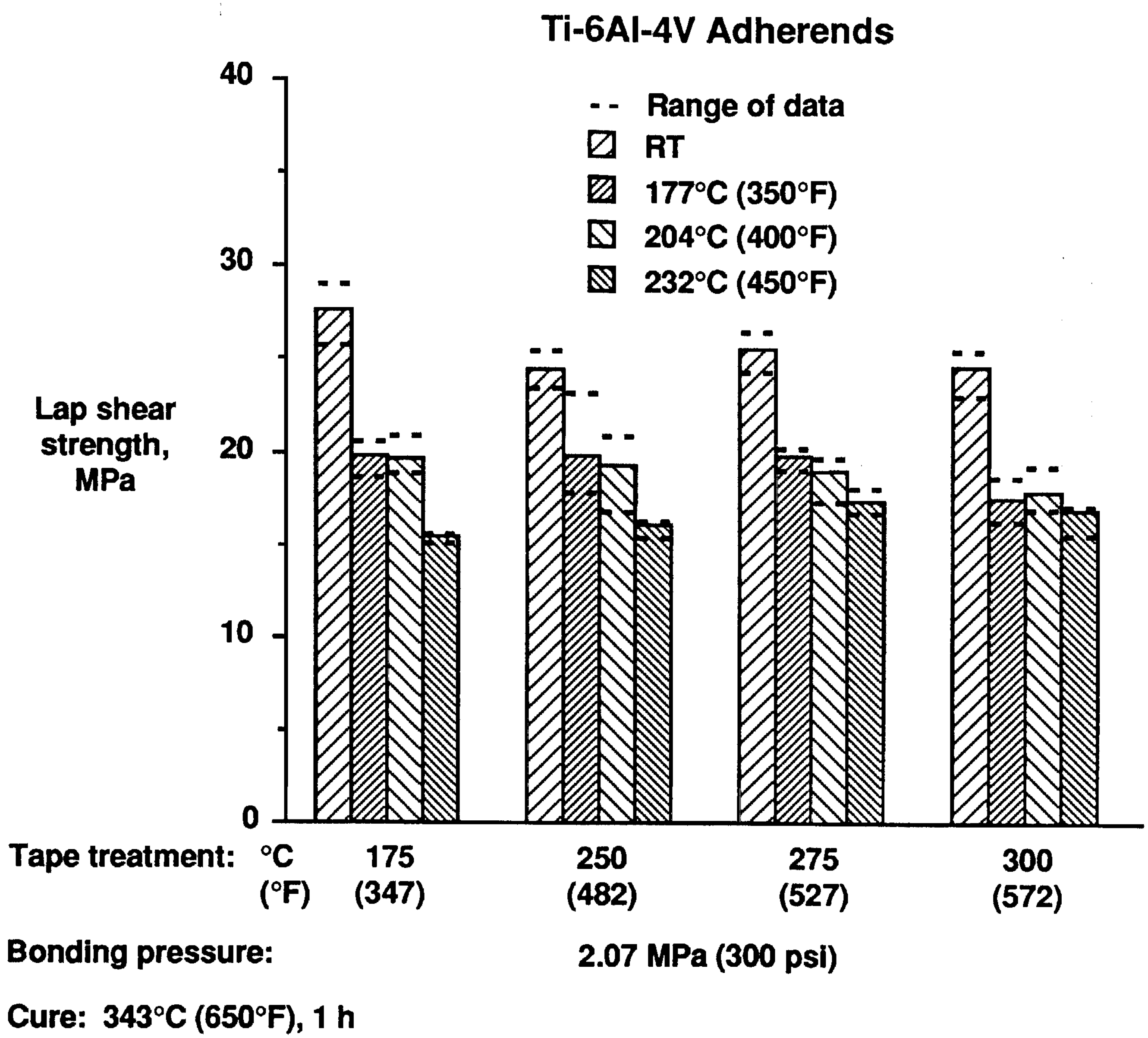


FIGURE 3. THE EFFECT OF TAPE HEAT TREATMENT PRIOR TO BONDING WITH 2.07 MPa (300 PSI) PRESSURE FOR TPI/C-PMDA BONDED Ti-6Al-4V.

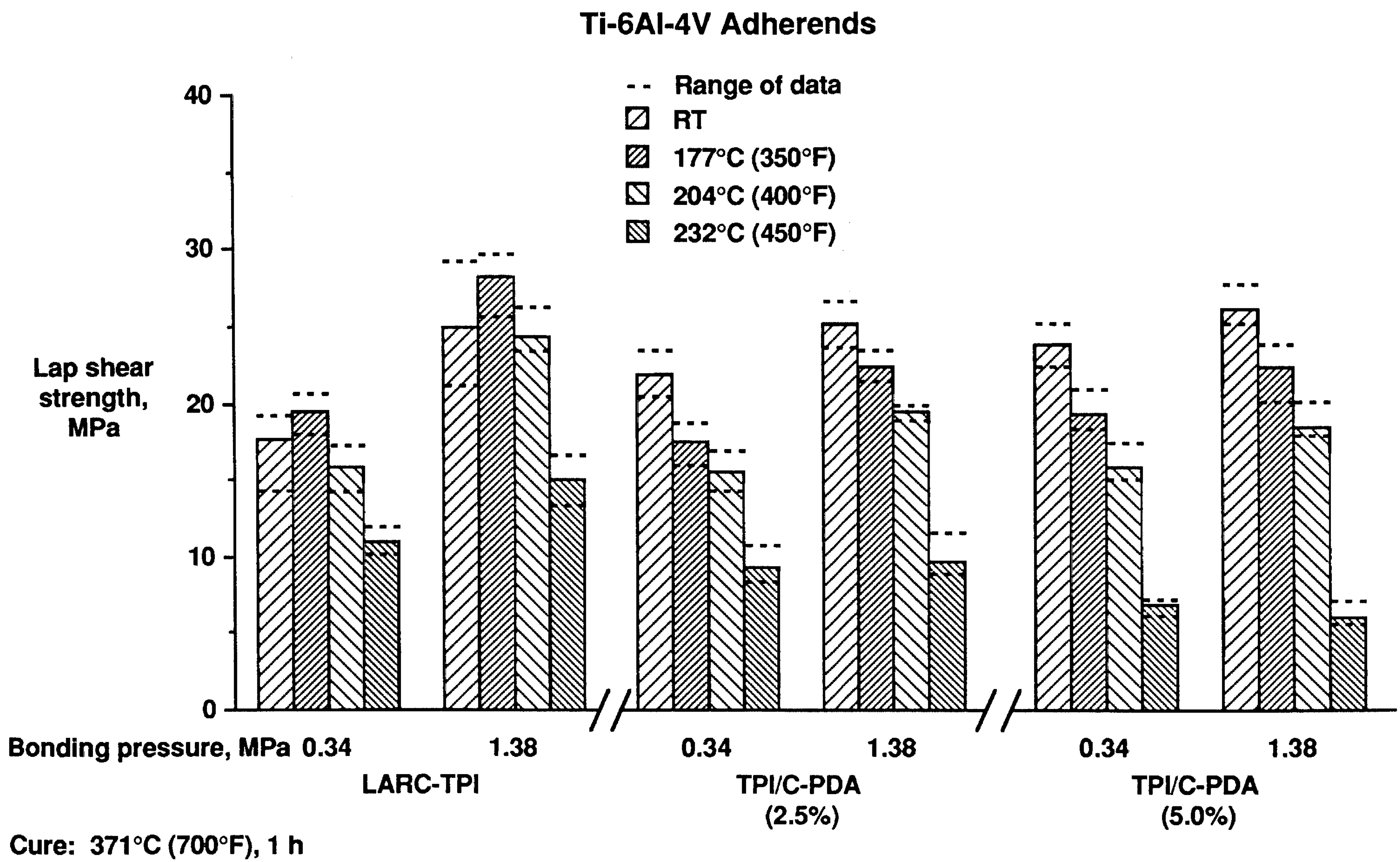


FIGURE 4. EFFECT OF BONDING PRESSURE ON LAP SHEAR STRENGTH FOR LARC-TPI, TPI/C-PDA (2.5%) AND TPI/C-PDA (5.0%) BONDED Ti-6Al-4V.

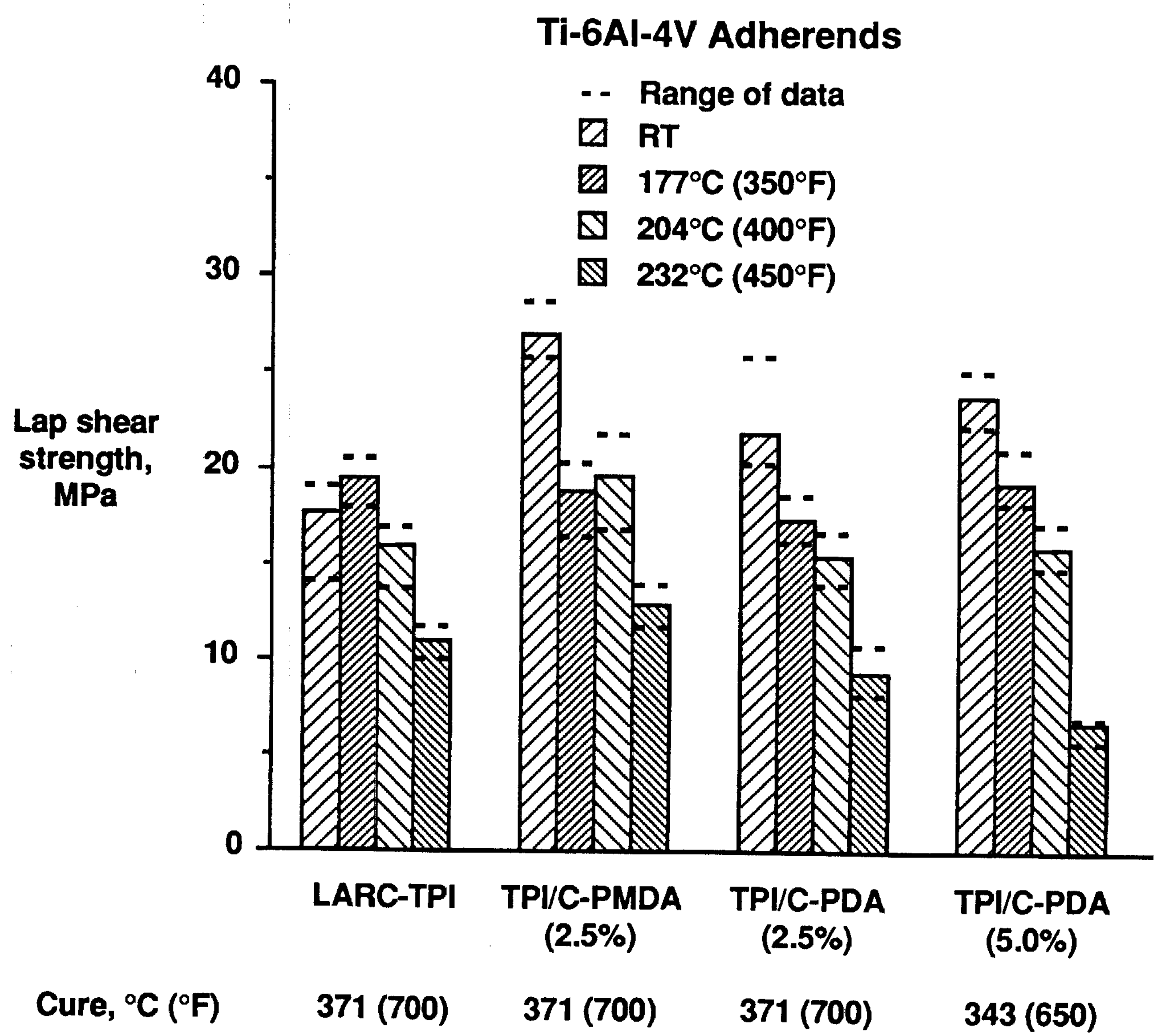
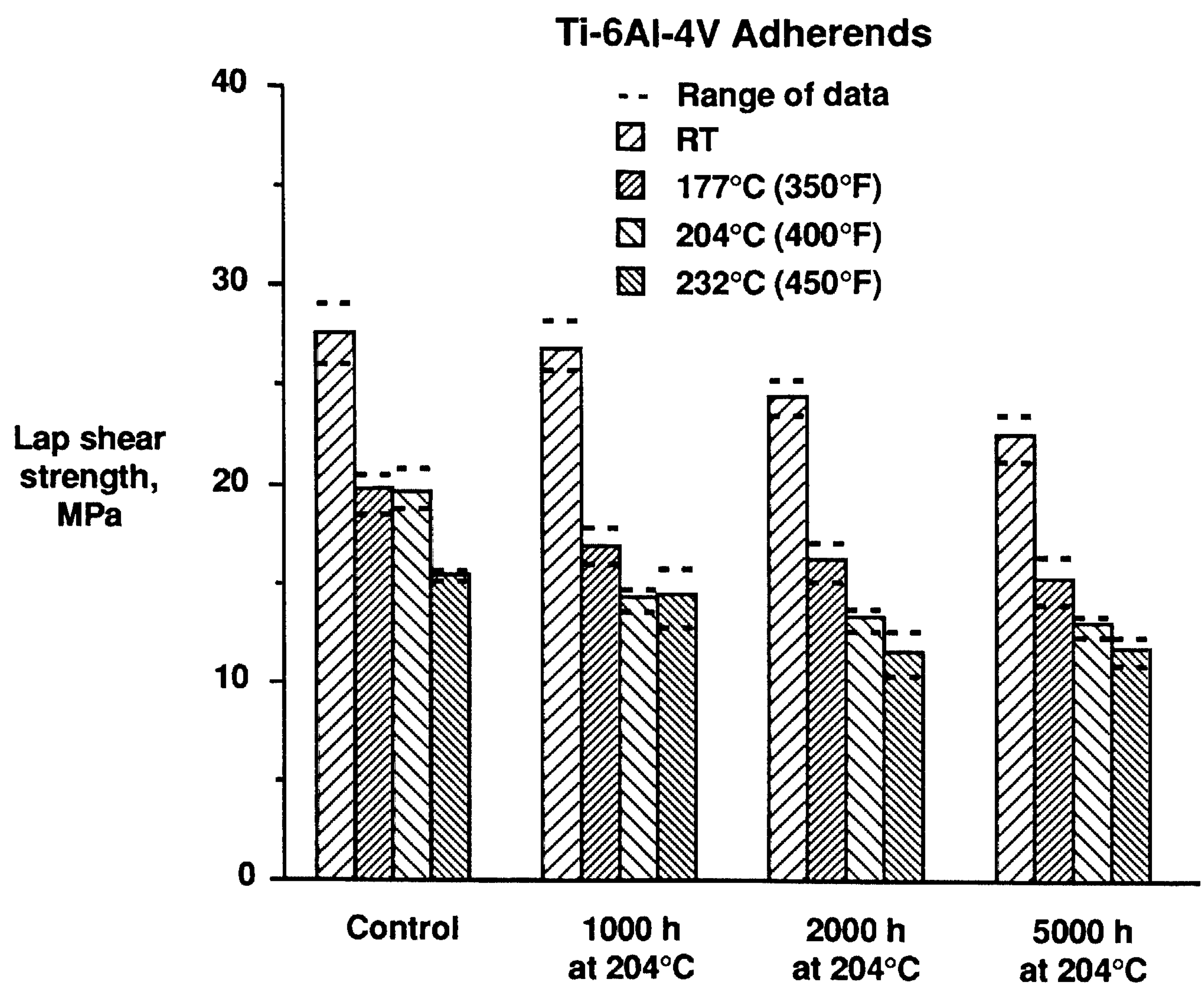
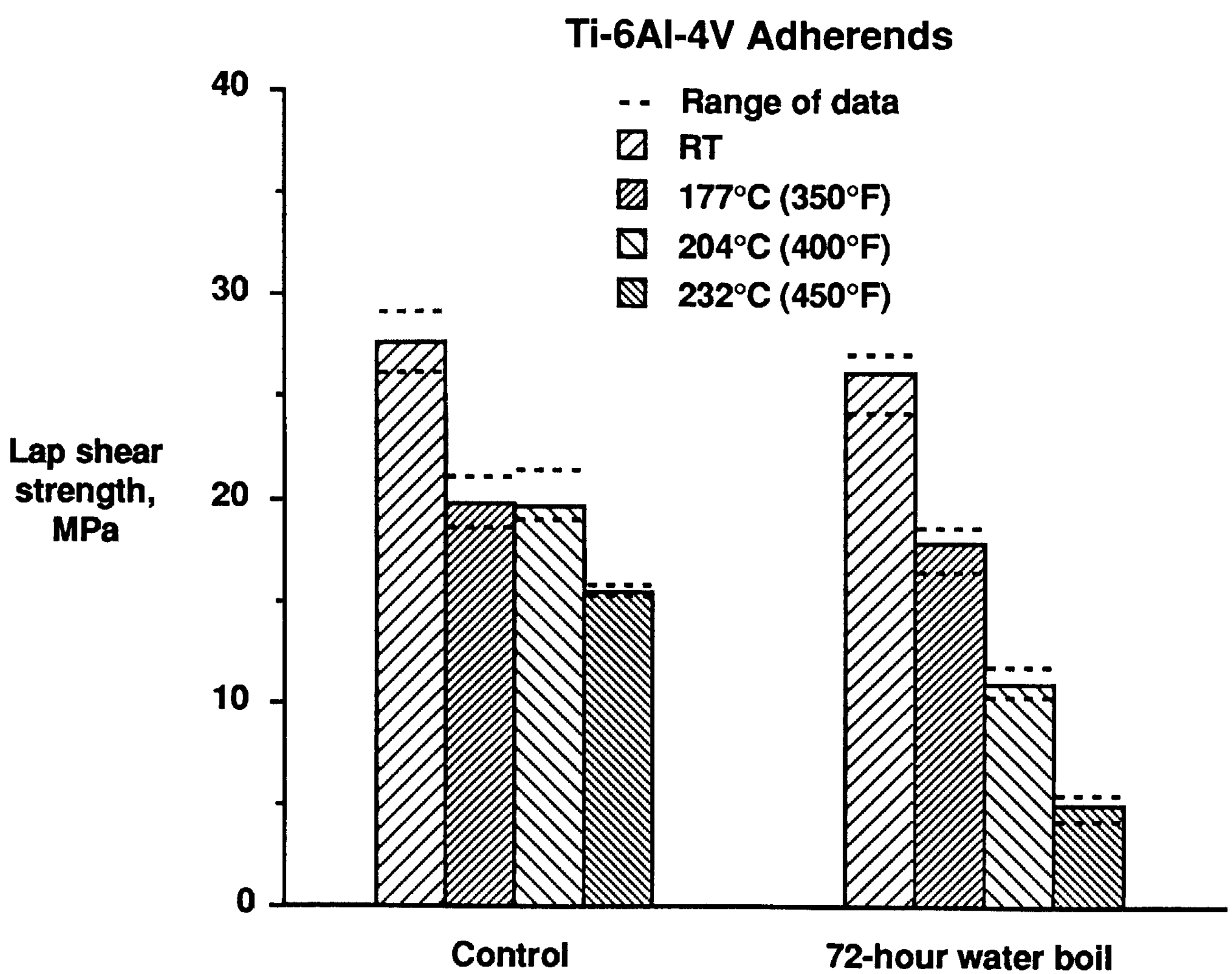


FIGURE 5. LAP SHEAR STRENGTHS FOR Ti-6Al-4V BONDED WITH LARC-TPI AND LARC-TPI WITH ADDITIVES USING 0.34 MPa (50 PSI) BONDING PRESSURE.



Cure: 2.07 MPa (300 psi), 343°C (650°F), 1 h

FIGURE 6. EFFECT OF THERMAL EXPOSURE IN AIR AT 204°C (400°F) FOR TPI/C-PMDA ADHESIVE BONDED Ti-6Al-4V.



Cure: 2.07 MPa (300 psi), 343°C (650°F), 1 h

FIGURE 7. EFFECT OF A 72-HOUR WATER BOIL ON LAP SHEAR STRENGTH FOR TPI/C-PMDA ADHESIVE BONDED Ti-6Al-4V.

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16. Abstract

Recent studies in our laboratory have shown that the processability of aromatic polyimides can be improved by the addition of bis(amide acids) or bisimides to LARC-TPI. These low molecular weight additives apparently lower the melt viscosity of aromatic polyimides without affecting the glass transition temperature. Well-consolidated, fiber reinforced composites have been fabricated using this technology. LARC-TPI can be processed as a thermoplastic polyimide to form high strength bonds, however, this is generally accomplished by processing at relatively high bonding pressures. The work reported is an adhesive investigation on the effects of two bisimide additives to LARC-TPI in an attempt to improve the bonding process by lowering the viscosity of the material to achieve improved bond strength properties. Apparently, the high flow which is exhibited by the additives when they melt, tended to be masked by the more viscous LARC-TPI.

17. Key Words (Suggested by Author(s))		18. Distribution Statement
Additives	LARC-TPI	Unclassified - Unlimited
Thermoplastic	High temperature	
Adhesive		Subject Category - 27
Lap shear strength		

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